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Reinvestigation of the Structure of the Trimethyltin Chloride 2,2'-Bipyridine Adduct

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The structure of the complex, $(CH_3)_3SnCl\cdot bipy$, was determined in the solid state using infrared and Mössbauer spectroscopies and in solution using the proton magnetic resonance spectrum recorded in CCl_4. The infrared and Mössbauer spectra indicated that, in the solid, the complex is a trigonal bipyramidal structure with coplanar methyl groups based on the quadrupole splitting values and the absence of the Sn–C symmetric vibration in the infrared spectrum. Upon dissolving in CCl_4, the structure is altered. The ^1H NMR spectrum indicated that dissociation occurred upon dissolution based on the low value of the tin methyl hydrogen coupling constant.

Introduction

Alkyltin halides have been reported [1] to form 1:1 adducts with 2,2'-bipyridine. It was proposed that these adducts are six coordinated monomers in non-polar solvents and in the solid state. Clark *et al.* [2], however, have suggested that the trimethyltin halide adducts may be indeed five coordinated with an ionic type structure. To resolve this difference, we have reinvestigated the structure of trimethyltin chloride-2,2'-bipyridyl both in solution and in the solid state using infrared, Mössbauer and proton magnetic resonance spectroscopies.

Experimental

The adduct was prepared according to the method of Clark and Williams [2] and its melting point was in agreement with the literature value.

The proton magnetic resonance spectrum was recorded in CCl_4 using the Varian Model EM-360 spectrometer.

The infrared spectrum of the solid adduct in a Nujol mull was measured using a Nicolet Model MX-1, and the solution spectrum in CCl_4 was measured on a Perkin-Elmer Model 337 spectrophotometer using polyethylene cells.

The Mössbauer spectrum was measured using a constant acceleration spectrometer [3] with moving source geometry. The source was 1 mCi $Ba^{119m}SnO_3$, and all parameters were measured related to the source. The parameters were obtained by fitting the spectrum to the best least-squares Lorentzian using a computer fitting program [4]. The powdered sample was measured at liquid nitrogen temperature using a cryostat described by Travis and Spijkerman [5].

Results and Discussion

The ratio of the quadrupole splitting to the isomer shift in the Mössbauer spectrum, p, has been used to determine the structure of similar complexes [6]. Generally, it has been found that complexes of tin(IV) with ρ values greater than 2.1 have coordination numbers greater than 4 [6]. Complexes of $(CH_3)_3SnCl$ are known to be five-coordinated, and their ρ values are in the range of 2.3 to 2.5 [7]. Thus, the observed ρ value of 2.56 (3.46 mm/s/1.35 mm/s) for the solid adduct indicates a pentacoordinated structure (Fig. 1). Furthermore, the observed quadrupole splitting of 3.46 mm/s (Fig. 1) is in the range (2.76–3.86 mm/s) found with trigonal bipyramidal complexes with axial ligands [6].

The absorption bands of the tin carbon vibrations further supports the pentacoordinated structure. The IR spectrum of the complex showed two bands in the tin carbon asymmetric stretching region at 554 and 544 cm^{-1}, which is in agreement with the earlier work [1]. However, neither of these vibrations can be assigned to the tin carbon symmetric mode which occurs around 514 cm^{-1} [8]. The absence of the tin carbon symmetric vibration indicates that the structure of the complex in the solid state must have

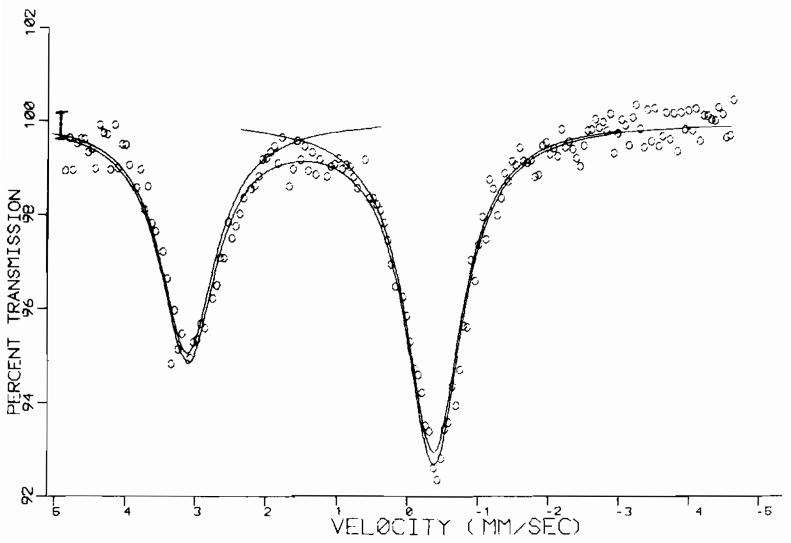


Fig. 1. Mössbauer spectrum for solid $(CH_3)_3SnCl \cdot bipy$ at liquid nitrogen temperature.

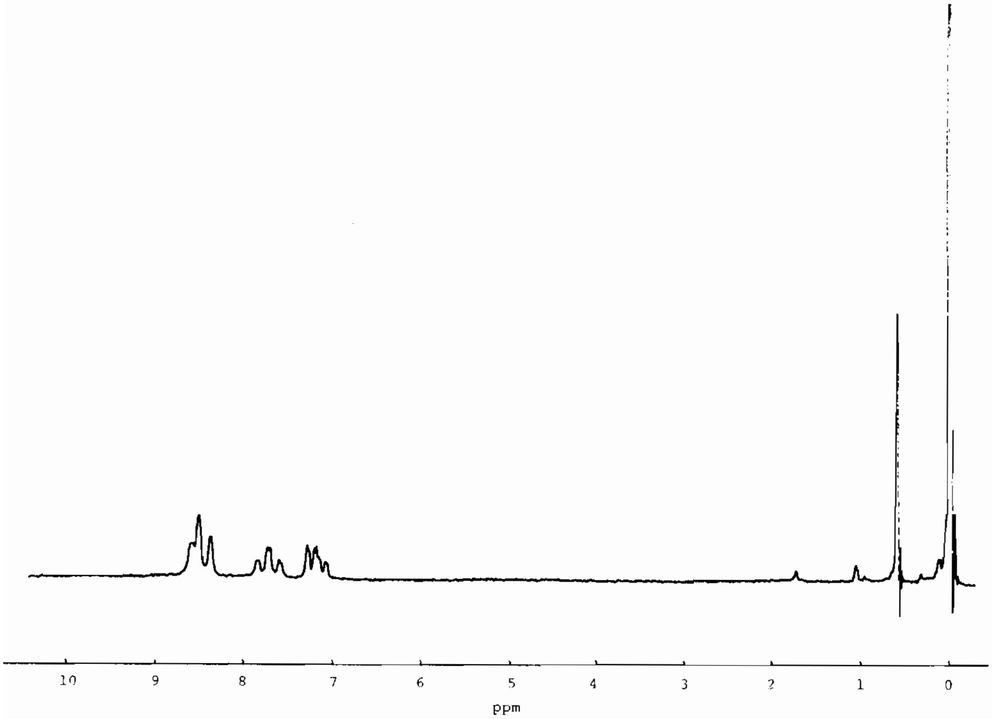
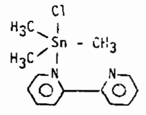


Fig. 2. ^1H NMR spectrum for $(CH_3)_3SnCl \cdot bipy$ recorded in CCl_4.

coplanar methyl groups. Therefore, the spectroscopic data indicate that the structure for the trimethyltin chloride adduct in the solid state must be trigonal bipyramidal with coplanar methyl groups with the bipyridine coordinate through one nitrogen atom as:



To determine if the structure in non-polar solvents was altered upon dissolution, the ^1H NMR and IR spectra were measured. A coupling constant of 58.4 Hz was measured for the ^{119}Sn methyl hydrogen in CCl_4 (Fig. 2). The tin methyl hydrogen spin–spin coupling constant has been correlated with the s-electron density around the tin atom by Holmes and Kaesz [9] and has been used to determine structures in similar compounds [10, 11]. Using this criterion, the observed value of 58.4 Hz for the tin methyl hydrogen coupling constant indicates sp^3 hybridization for the tin atom. This reaffirms the earlier suggestion [1] that, in solution, dissociation takes place, and the complex breaks down to the starting materials, trimethyltin chloride and 2,2′-bipyridine.

This is further supported by the IR spectrum of the solution. In CCl_4, the tin carbon symmetric vibration at 515 cm^{-1} is observed as well as the asymmetric vibration at 550 cm^{-1}.

The trimethyltin chloride–2,2′-bipyridine adduct in the solid state is trigonal bipyramidal with coplanar methyl groups and dissociates upon solution. Since the other halides, bromide and iodide, have very similar absorption spectra in the 500–600 cm^{-1} region [2], it is reasonable to presume that the structure of these adducts in the solid state is the same as the chloride complex.

Acknowledgments

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